Introduction to Mass Spectrometry

Third Edition

J. Throck Watson, Ph.D.

Professor, Departments of Biochemistry and Chemistry
Michigan State University
East Lansing, Michigan

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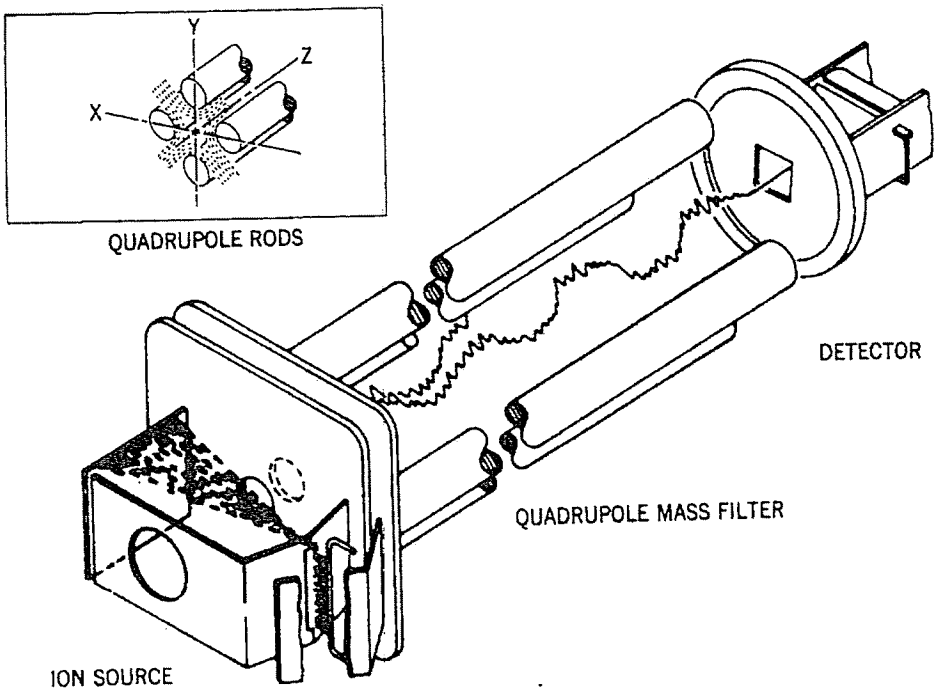

FIG. 4.7. Schematic diagram of quadrupole mass spectrometer illustrating irregular flight path of ions from the ion source through the central space between the quadrupole rods to the detector. (Courtesy of Finnigan Corporation.)

B. Equations of Motion Within the Quadrupole

A rigorous examination of the trajectory of ions through the quadrupole *m/z* filter necessarily takes into account a large number of physical variables that affect the instantaneous electric fields "seen" by the ions. For the classical hyperbolic mass filter, the potential distribution *(F)* at any time *(t)* is described by the following equation:

$$\Phi = [U + VCos(\omega t)]\frac{x^2 - y^2}{2r_0^2} \tag{4.5}$$

where x and y are the distances along the coordinate axes, r_o is the distance from the z axis in Fig. 4.7 to either of the quadrupole surfaces, A is the angular frequency ($2\pi f$) of the applied alternating-current (AC) signal, V is the magnitude of the applied RF signal, and U is the magnitude of the DC potential applied to the surfaces.

The instantaneous electric field along any of the three axes *(x-y-z)* in Fig. 4.7, can be computed by taking the partial derivative of the expression above (Eq. 4.5) as a function of a particular axis. This exercise shows the useful result that the applied DC and AC potentials to the surfaces impress no acceleration on the ions

in the Z direction, that is, along the axis between the ion source and the detector, because the general formula for the potential shows no dependence on the term Z.

Definition of the a and q terms allows the Mathieu equations (18,19) to be somewhat simplified; a is related to DC and q is related to RF. From the standpoint of the quadrupole mass spectrometer, a bounded solution to the Mathieu equation corresponds to a finite displacement of the ion along the x or y axis. That is, the ion follows a trajectory that avoids collision with the surfaces and eventually reaches the detector. The other general class of solutions, the unbounded solution, describes the situation in which the radial displacement of the ion increases without bound, and therefore it collides (is "filtered out") with the surfaces to preclude transmission through the quadrupole to the detector.

$$a_x = -a_y = 4zeU/m^2r_0^2 \tag{4.6}$$

$$q_x = -q_y = 2zeV/m^2r_0^2 \tag{4.7}$$

The ions for which there is a bounded solution have a and q values that correspond to *stable trajectories* in the quadrupole mass filter. These stable trajectories allow the ion to be transmitted from the ion source to the detector without collision with the surfaces of the quadrupole filter. Stable coordinates of a and q space are those in the shaded area of the a-q diagram in Fig. 4.8.

The mathematical transformations that lead to the formation of the a-q diagram serve a useful purpose in simplifying the complex array of parameters that affect motion of the ion in the quadrupole mass filter. In general, the stability diagram as shown in Fig. 4.8 is a two-dimensional plot showing how the six-dimensional problem (involving e, ω, r_o, m, U, and V) can be reduced to a two-dimensional problem involving only the mathematically reduced a and q parameters.

C. Stability Diagram

Two important points can be made while viewing Fig. 4.8. First, if the quadrupole is operated with a DC potential and an RF amplitude that define the operating line in the stability diagram (18,20), only those ions with m/z values defined by the (a-q) space coordinates at the tip of the diagram will have stable trajectories (22). If the DC:RF ratio is adjusted to raise the operating line even higher, the resolving power of the instrument increases, but the sensitivity decreases because fewer ions follow a stable trajectory to reach the detector. The second point relates to "RF-only" operation of a quadrupole. In the RF-only mode, there is no DC field; thus, $a = 0$ [$U = 0$ in Eq. (4.5)]. Therefore, the operating line lies horizontally along the abscissa, indicating theoretically that ions of all m/z values have stable trajectories and are transmitted through the quadrupole filter.

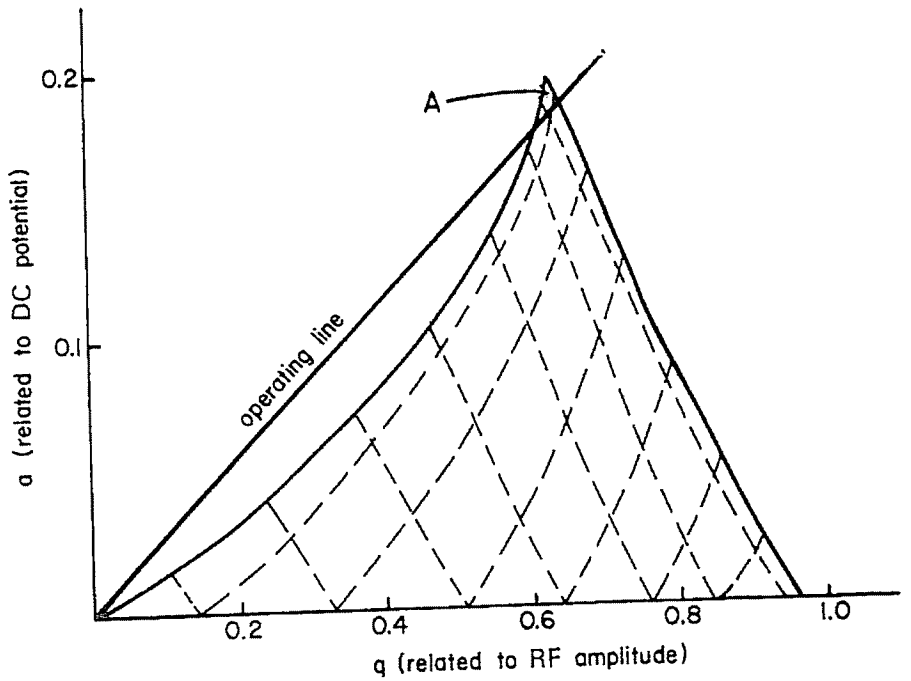

FIG. 4.8. Stability diagram of (**a-q**) space showing regions *(patchwork area)* that correspond to mathematically stable ion trajectories in the quadrupole mass spectrometer. Area **A** indicates region of stability limited by the operating line (established by ratio of DC:RF potentials) of the instrument.

As might be anticipated from the very large number of a and q values that constitute the shaded area in the stability diagram, a quadrupole mass filter could, in principle, be operated at any value in the a-q space corresponding to a point in the shaded region. However, in practice, the values of a and q space are limited by adjusting the RF and DC potentials to a fixed ratio. In fact, in the typical quadrupole mass spectrometer, the DC voltage is held at a fixed fraction of the RF voltage. This fixed ratio leads to an operating mass scan line with a slope of 2 U/V, which is shown at the approximately 45° angle in Fig. 4.8 of the stability diagram. By fixing the ratio of RF and DC potentials to establish the resolving power, the only values of a and q space available to ions in the instrument lie along the operating line within the shaded region. That is, a circumstance in which ions of m/z 300 would be transmitted through the quadrupole, but ions of m/z 299 and lower and ions of m/z 301 and higher would not be transmitted. The complete mass spectrum is obtained by scanning the magnitude of RF *(V)* and DC potential *(U)* through increasing or decreasing values. As explained in previous equations, the mass of an ion is inversely proportional to both a and q; thus, by scanning the magnitude of RF and DC potentials from a low to a high value, ions of increasing mass will sequentially take on stable values of a and q space and be transmitted to the detector.

Mass spectrometry

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Mass spectrometry is an analytical technique which determines the mass-to-charge (m/z) ratio of ions. It is most generally used to find the composition of a physical sample by generating a mass spectrum representing the masses of the components of a sample. It has several broad applications:

1. Identifying unknown compounds by the mass of the compound and/or fragments thereof.
2. Determining the isotopic composition of one or more elements in a compound.
3. Determining the structure of compounds by observing the fragmentation of the compound.
4. Quantitating the amount of a compound in a sample using carefully designed methods (mass spectrometry is not inherently quantitative).
5. Studying the fundamentals of gas phase ion chemistry (the chemistry of ions and neutrals in vacuum).
6. Determining other physical, chemical or even biological properties of compounds with a variety of other approaches.

A **mass spectrometer** is a device used for mass spectrometry, and produces a mass spectrum of a sample to find its composition. This is normally achieved by ionizing the sample and separating ions of differing masses and recording their relative abundance by measuring intensities of ion flux. A typical mass spectrometer comprises three parts: an ion source, a mass analyzer, and a detector.

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How it works in layman terms

Different molecules have different masses, and this fact is used in a mass spectrometer to determine what molecules are present in a sample. For example, table salt (NaCl), is vaporized (turned into gas) and broken down (ionized) into electrically charged particles, called ions, in the first part of the mass spectometer. The sodium ions

and chloride ions have specific molecular weights. They also have a charge, which means that they will be moved under the influence of an electric field. These ions are then sent into an ion acceleration chamber and passed through a slit in a metal sheet. A magnetic field is applied to the chamber, which pulls on each ion equally and deflects them (makes them curve instead of travelling straight) onto a detector. The lighter ions deflect further than the heavy ions because the force on each ion is equal but their masses are not (this is derived from the equation $F = ma$ which states that if the force remains the same, the mass and acceleration are inversely proportional). The detector measures exactly how far each ion has been deflected, and from this measurement, the ion's 'mass to charge ratio' can be worked out. From this information it is possible to determine with a high level of certainty what the chemical composition of the original sample was.

This example was of a sector instrument, however there are many types of mass spectrometers that not only analyze the ions differently but produce different types of ions; however they all use electric and magnetic fields to change the path of ions in some way.

Instrumentation

Ion source

The ion source is the part of the mass spectrometer that ionizes the material under analysis (the analyte). The ions are then transported by magnetic or electrical fields to the mass analyzer.

Techniques for ionization have been key to determining what types of samples can be analyzed by mass spectrometry. Electron ionization and chemical ionization are used for gases and vapors. In chemical ionization sources, the analyte is ionized by chemical ion-molecule reactions during collisions in the source. Two techniques often used with liquid and solid biological samples include electrospray ionization (due to John Fenn) and matrix-assisted laser desorption/ionization (MALDI, due to M. Karas and F. Hillenkamp). Inductively coupled plasma sources are used primarily for metal analysis on a wide array of samples types. Others include fast atom bombardment (FAB), thermospray, atmospheric pressure chemical ionization (APCI), secondary ion mass spectrometry (SIMS) and thermal ionisation.

Mass analyzer

Mass analyzer separate the ions according to their mass per charge (m/z). There are many types of mass analyzers. Usually they are categorized based on the principles of operation.

Sector MS: It uses an electric and/or magnetic field to affect the path and/or velocity of the charged particles in some way. The force exerted by electric and magnetic fields are defined by the Lorentz force law:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}),$$

where **E** is the electric field strength, **B** is the magnetic field induction, q is the charge of the particle, **v** is its current velocity (expressed as a vector), and × is the cross product. All mass analyzers use the Lorentz forces in some way either statically or dynamically in mass-to-charge determination.

As shown above, sector instruments change the direction of ions that are flying through the mass analyzer. The ions enter a magnetic or electric field which bends the ion paths depending on their mass-to-charge ratios (m/z), deflecting the more charged and faster-moving, lighter ions more. The ions eventually reach the detector and their relative abundances are measured. The analyzer can used to select a narrow range of m/z's or to scan through a range of m/z's to catalog the ions present.

Besides the original magnetic-sector analyzers, several other types of analyzer are now more common, including time-of-flight, quadrupole ion trap, quadrupole and Fourier transform ion cyclotron resonance mass analyzers.

TOFMS: Perhaps the easiest to understand is the Time-of-flight (TOF) analyzer. It boosts ions to the same kinetic energy by passage through an electric field and measures the times they take to reach the detector. Although the kinetic energy is the same, the velocity is different so the lighter more highly charged ion will reach the detector first.

QMS: Quadrupole mass analyzers use oscillating electrical fields to selectively stabilize or destabilize ions passing through a RF quadrupole field.

QIT: The quadrupole ion trap works on the same physical principles as the QMS, but the ions are traped and sequentially ejected. Ions are created and trapped in a mainly quadrupole RF potential and separated by m/z, non-destructively or destructively. There are many mass/charge separation and isolation methods but most commonly used is the mass instability mode in which the RF potential is ramped so that the orbit of ions with a mass $a > b$ are stable while ions with mass b become unstable and are ejected on the z-axis onto a detector. The cylindrical ion trap mass spectrometer is a derivative of the quadrupole ion trap mass spectrometer.

See also the main article on quadrupole ion trap mass spectrometer

Linear QIT: In the linear quadrupole ion trap the ions are trapped in a 2D quadrupole filed instead of the 3D quadrupole field of the QIT.

FTMS: Fourier transform mass spectrometry measures mass by detecting the image current produced by ions cyclotroning in the presence of a magnetic field. Instead of measuring the deflection of ions with a detector such as a electron multiplier, the ions are injected into a Penning trap (a static electric/magnetic ion trap) where they effectively form part of a circuit. Detectors at fixed positions in space measure the electrical signal of ions which pass near them over time producing cyclical signal. Since the frequency of the ions' cycling is determined by its mass to charge ratio, this can be deconvoluted by performing a Fourier transform on the signal. FTMS has the advantage of improved sensitivity (since each ion is 'counted' more than once) as well as much higher resolution and thus precision.

See also the main article on Fourier transform ion cyclotron resonance

Each analyzer type has its strengths and weaknesses. In addition, there are many more less common mass analyzers.

Many mass spectrometers use two or more mass analyzers for tandem mass spectrometry (MS/MS).

Detector

The final element of the mass spectrometer is the detector. The detector records the charge induced or current produced when an ion passes by or hits a surface. In a scanning instrument the signal produced in the detector during the course of the scan versus where the instrument is in the scan (at what m/z) will produce a mass spectrum, a record of how many ions of each *m/z* are present.

Typically, some types of electron multiplier is used, though other detectors (such as Faraday cups) have been used. Because the number of ions leaving the mass analyzer at a particular instant is typically quite small, significant amplification is often necessary to get a signal. Microchannel Plate Detectors are commonly used in

modern commercial instruments. In FTMS, the detector consists of a pair of metal plates within the mass analyzer region which the ions only pass near. No DC current is produced, only a weak AC image current is produced in a circuit between the plates.

Hyphenated MS

Gas chromatography/MS

See also the main article on Gas chromatography-mass spectrometry

A common form of mass spectrometry is gas chromatography-mass spectrometry (GC/MS or GC-MS). In this technique, a gas chromatograph is used to separate compounds. This stream of separated compounds is fed on-line into the ion source, a metallic filament to which voltage is applied. This filament emits electrons which ionize the compounds. The ions can then further fragment, yielding predictable patterns. Intact ions and fragments pass into the mass spectrometer's analyser and are eventually detected.

Liquid chromatography/MS

See also the main article on Liquid chromatography-mass spectrometry

Similar to gas chromatography MS (GC/MS), liquid chromatography mass spectrometry (LC/MS or LC-MS) separates compounds chromatographically before they are introduced to the ion source and mass spectrometer. It differs from GC/MS in that the mobile phase is liquid, usually a combination of water and organic solvents, instead of gas. Most commonly, an electrospray ionization source is used in LC/MS.

IMS/MS

Ion mobility spectrometry/mass spectrometry is a technique where ions are first separated by drift time through some pressure of neutral gas given an electrical potential gradient before being introduced into a mass spectrometer. The drift time is a measure of the radius relative to the charge of the ion. The duty cycle of IMS (time over which the experiment takes place) is longer than most mass spectrometers such that the mass spectrometer can sample along the course of the IMS separation. This produces data about the IMS separation and the mass-to-charge ratio of the ions in a manner similar to LC/MS. Note, however, that the duty cycle of IMS is short relative to liquid chromatography or gas chromatography separations and can thus be coupled to such techniques producing triply hyphenated techniques such as LC/IMS/MS.

Tandem MS (MS/MS)

Tandem mass spectrometry involves multiple steps of mass selection or analysis, usually separated by some form of fragmentation. A tandem mass spectrometer is one capable of multiple rounds of mass spectrometry. For example, one mass analyzer can isolate one peptide from many entering a mass spectrometer. A second mass analyzer then stabilizes the peptide ions while they collide with a gas, causing them to fragment by collision-induced dissociation (CID). A third mass analyzer then catalogs the fragments produced from the peptides. Tandem MS can also be done in a single mass analyzer over time as in a quadrupole ion trap. There are various methods for fragmenting molecules for tandem MS, including collision-induced dissociation (CID), electron capture dissociation (ECD), infrared multiphoton dissociation (IRMPD) and blackbody infrared radiative dissociation (BIRD).

Applications

Isotope ratio MS

Mass spectrometry is also used to determine the isotopic composition of elements within a sample. Differences in mass among isotopes of an element are very small, and the less abundant isotopes of an element are typically very rare, so a very sensitive instrument is required. These instruments, sometimes referred to as isotope ratio mass spectrometers (IR-MS), usually use a single magnet to bend a beam of ionized particles towards a series of Faraday cups which convert particle impacts to electric current. A fast on-line analysis of deuterium content of water can be done using Flowing afterglow mass spectrometry, FA-MS. Probably the most sensitive and accurate mass spectrometer for this purpose is the accelerator mass spectrometer (AMS). Isotope ratios are important markers of a variety of processes. Some isotope ratios are used to determine the age of materials for example as in carbon dating.

Trace Gas Analysis

Several techniques use ions created in a dedicated ion source injected into a flow tube or a drift tube: selected ion flow tube (SIFT-MS), and proton transfer reaction (PTR-MS), are variants of chemical ionization dedicated for trace gas analysis of air, breath or liquid headspace using well defined reaction time allowing calculations of analyte concentrations from the known reaction kinetics without the need for internal standard or calibration.

Pharmcokinetics

Pharmacokinetics is often studied using mass spectrometry due to the complex nature of the matrix (often blood or urine) and the need for high sensitivity to observe low dose and long time point data. The most common instrumentation used in this application is LC-MS with a triple quadrupole mass spectrometer. Tandem mass spectrometry is usually employed for added specificity. Standard curves and internal standards are used for quantitation of usually a single pharmaceutical in the samples. The samples represent different time points as a pharmaceutical is administered and then metabolized or cleared from the body. Blank or t=0 samples taken before administration are important in determining background and insuring data integrity with such complex sample matrices. Much attention is paid to the linearity of the standard curve however it is not uncommon to use curve fitting with more complex functions such as quadratics since the response of most mass spectrometers is less than linear across large concentration ranges.

Mass spectrometry of proteins

Mass spectrometry is an important emerging method for the characterization of proteins. The two primary methods for ionization of whole proteins are electrospray ionization and matrix-assisted laser desorption ionization (MALDI). In keeping with the performance and mass range of available mass spectrometers, two approaches are used for characterizing proteins. In the first, intact proteins are ionized by either of the two techniques described above, and then introduced to a mass analyser. In the second, proteins are enzymatically digested into smaller peptides using an agent such as trypsin or pepsin. Other proteolytic digest agents are also used. The collection of peptide products are then introduced to the mass analyser. This is often referred to as the "bottom-up" approach of protein analysis.

Whole protein mass analysis is primarily conducted using either time-of-flight (TOF) MS, or Fourier transform ion cyclotron resonance. These two types of instrument are preferable here because of their wide mass range, and in the case of FT-ICR, its high mass accuracy. Mass analysis of proteolytic peptides is a much more popular

method of protein characterization, as cheaper instrument designs can be used for characterization. Additionally, sample preparation is easier once whole proteins have been digested into smaller peptide fragments. The most widely used instrument for peptide mass analysis is the quadrupole ion trap. Multiple stage quadrupole-time-of-flight and MALDI time-of-flight instruments also find use in this application.

Protein and peptide fractionation coupled with mass spectrometry

Proteins of interest to biological researchers are usually part of a very complex mixture of other proteins and molecules that co-exist in the biological medium. This presents two significant problems. First, the two ionization techniques used for large molecules only work well when the mixture contains roughly equal amounts of constituents, while in biological samples, different proteins tend to be present in widely differing amounts. If such a mixture is ionized using electrospray or MALDI, the more abundant species have a tendency to "drown" signals from less abundant ones. The second problem is that the mass spectrum from a complex mixture is very difficult to interpret due to the overwhelming number of mixture components. This is exacerbated by the fact that enzymatic digestion of a protein gives rise to a large number of peptide products.

To contend with this problem, two methods are widely used to fractionate proteins, or their peptide products from an enzymatic digestion. The first method fractionates whole proteins and is called two-dimensional gel electrophoresis. The second method, high performance liquid chromatography is used to fractionate peptides after enzymatic digestion. In some situations, it may be necessary to combine both of these techniques.

Gel spots identified on a 2D Gel are usually attributable to one protein. If the identity of the protein is desired, the gel spot can be excised, and digested proteolytically. The peptide masses resulting from the digestion can be determined by mass spectrometry using peptide mass fingerprinting. If this information does not allow unequivocal identification of the protein, its peptides can be subject to tandem mass spectrometry.

Characterization of protein mixtures using HPLC/MS is also called *shotgun proteomics* and *mudpit*. A peptide mixture that results from digestion of a protein mixture is fractionated by one or two steps of liquid chromatography. The eluent from the chromatography stage can be either directly introduced to the mass spectrometer through electrospray ionization, or laid down on a series of small spots for later mass analysis using MALDI.

Protein identification

There are two main ways MS is used to identify proteins. Peptide mass fingerprinting (mentioned in the previous section) uses the masses of proteolytic peptides as input to a search of a database of predicted masses that would arise from digestion of a list of known proteins. If a protein sequence in the reference list gives rise to a significant number of predicted masses that match the experimental values, there is some evidence that this protein was present in the original sample.

Tandem MS is becoming a more popular experimental method for identifying proteins. Collision-induced dissociation is used in mainstream applications to generate a set of fragments from a specific peptide ion. The fragmentation process primarily gives rise to cleavage products that break along peptide bonds. Because of this simplicity in fragmentation, it is possible to use the observed fragment masses to match with a database of predicted masses for one of many given peptide sequences. Tandem MS of whole protein ions has been investigated recently using electron capture dissociation and has demonstrated extensive sequence information in principle but is not in common practice. This is sometimes referred to as the "top-down" approach in that it involves starting with the whole mass and then pulling it apart rather than starting with pieces (proteolytic fragments) and piecing the protein back together using De novo repeat detection (bottom-up).

History

The first mass spectrography technique was described in an 1899 article by English scientist J.J. Thomson. The processes that more directly gave rise to the modern version were devised by Arthur Jeffrey Dempster and F.W. Aston in 1918 and 1919 respectively.

In 2002, the Nobel Prize in Chemistry was received by John Fenn for the development of electrospray ionization (ESI) and Koichi Tanaka for the development of soft laser desorption (SLD) in 1987. An improved SLD method, matrix-assisted laser desorption/ionization (MALDI), was developed by Franz Hillenkamp and Michael Karas in 1988. The choice of Tanaka to recieve the nobel prize for this work over Hillenkamp and Karas is a contentious issue to some people in the field. The two methodologies are remarkably similiar yet significantly different. The work of Hillenkamp and Karas is fundamentally the same as the current implementation of matrix-assisted laser desorption/ionization which is now ubiqitous in mass spectrometry. Hillenkamp and Karas also demonstrated exceptionally well the importance of this new technique. On the other hand the work of Tanaka is similar and published significantly earlier such that the work of Hillenkamp and Karas could in theory be a derivative improvement. Yet, the work of Tanaka on SLD may have never come to prominence or become particularly useful without futher improvement.

See also

- Electron spectrometer
- Blackbody infrared radiative dissociation
- Calutron
- Chemical ionization
- Collision-induced dissociation
- Electron capture dissociation
- Electron ionization
- Electron multiplier
- Electrospray ionization
- Faraday cup
- Fourier transform ion cyclotron resonance
- Gas chromatography-mass spectrometry
- Helium mass spectrometer
- ICP-MS
- Infrared multiphoton dissociation
- Ion source
- Liquid chromatography-mass spectrometry
- Mass spectrum
- Matrix-assisted laser desorption/ionization
- Microchannel plate detector
- Quadrupole ion trap
- Quadrupole mass analyzer
- SIFT-MS selected ion flow tube mass spectrometry
- Secondary ionisation
- Sector instrument
- Taylor cone
- Thermal ionisation
- Time-of-flight

External links

- American Society for Mass Spectrometry (http://www.asms.org/)
- Australian and New Zealand Society for Mass Spectrometry (http://www.latrobe.edu.au/anzsms/)
- British Mass Spectrometry Society (http://www.bmss.org.uk/)
- Canadian Society for Mass Spectrometry (http://www.csms.inter.ab.ca/)
- International Mass Spectrometry Society (http://www.imss.nl/)
- A History of Mass Spectrometry (Scripps) (http://masspec.scripps.edu/information/history/)
- Mass spectrometer simulation (http://www.vias.org/simulations/simusoft_msscope.html) An interactive application simulating the console of a mass spectrometer
- Mass spectrometry terms wiki (http://www.msterms.com/wiki/)
- Self-test (http://www.chem.arizona.edu/quizplease/msintro/aldehyd/aldehyd.htm#begin)

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Ion/molecule reactions, mass spectrometry and optical spectroscopy in a linear ion trap

M. Welling[1a], H. A. Schuessler[b], R. I. Thompson[a], H. Walther[a,*]

[a]*Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching bei München, Germany*
[b]*Department of Physics, Texas A&M University, College Station, TX 77483, USA*

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Abstract

A linear-geometry, radio-frequency, quadrupole ion trap has been developed to generate, purify, accumulate and study atomic and molecular ions in the gas phase. By employing a trap-based system, both reactant and product ions can be stored for significant time periods, which can both enhance the efficiency of gas-phase reaction processes and create an environment to observe collision products after vibrational and rotational excitations have had time to relax. Relaxation occurs via viscous cooling with a dilute buffer gas or via laser cooling. Furthermore, the setup is particularly useful for performing optical spectroscopy on the trapped ions.

Atomic and molecular ovens are used to generate thermal beams of neutral species, which are then ionized by electron bombardment. The ions can be trapped, or they can be collided with neutral molecules (e.g. C_{60}) under well defined experimental conditions. The collision energies are variable over a range from nearly 0 to 200 eV. This feature makes possible studies of complex formation, charge transfer and collision-induced fragmentation as a function of kinetic energy. A wide range of masses of up to 4000 u can be stored and manipulated with this apparatus.

Two mass spectrometric techniques for the analysis of trapped ionic species are presented. In one method, parametric excitation of the secular motion is used to generate mass spectra with resolutions as high as 1 part in 800 with a simple experimental setup. The second method is capable of quickly generating mass spectra over the entire range of trapped masses, but has only moderate resolution. These spectra are generated by linearly sweeping the rf-trapping voltage to zero and detecting ions as their trap depth falls below a threshold value. In the trapping volume, which is 10 cm in length and 200 μm in diameter, 10^6 ions can be loaded and stored, corresponding to an ion density above 10^8 cm^{-3}. Such densities facilitate spectroscopy of the stored ions. Both laser-induced fluorescence and photodissociation measurements have been carried out with a cw laser system providing near-infrared, visible, and ultraviolet beams. Absolute, total cross-sections and branching ratios of the photodissociation of MgC_{60}^+ have been measured. © 1998 Elsevier Science B.V.

Keywords: Energy resolved collision processes; Fullerene complexes; Gas phase optical spectroscopy; Ion trap mass spectrometry; Parametric excitation of secular motion

1. Introduction

Gas phase, energy-resolved investigations of reaction products remain an experimental challenge in both physics and chemistry. Considerable efforts, therefore, are ongoing in this field due to the strong interest in many different reactions stemming from their dominant role in research areas such as the atmospheres of planets and stars, interstellar media, and plasma and fusion research. The pursuit of a fundamental

* Corresponding author.
[1] Present address: Department of Physics, Rice University, Houston, TX 77005, USA.

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theoretical understanding of ion–molecule processes in these areas has resulted in a need for data to be used in the development of models. These models are not only for simple two-, three- and four-particle systems, but also for clusters and large molecular complexes such as are found in the various fullerene structures. The ideal apparatus for generating the required data should allow for a state-specific study of the reaction dynamics of the collisions over a wide range of collision energies. Although there have been significant improvements in the last four decades, most of the presently available experimental instruments were designed for the solution of specific problems, with few being ideally suited for answering many or all of the questions of interest. Furthermore, in nature the interaction of atoms and molecules with photons often plays a key role in understanding specific properties and reaction processes. In this situation optical spectroscopy provides a powerful general tool to advance the present knowledge due to its high sensitivity, state specificity, and ability to initiate photon-induced processes.

This paper describes a compact ion trap system suitable for the generation, purification, storage and analysis of ionic collision products, all carried out in the gas phase. The analysis techniques include both mass spectrometry and optical spectroscopy. The apparatus is depicted in Fig. 1. In general, ion/molecule apparatuses fall into one of two general categories, guided ion beams [1–3] or ion traps [4] of the Penning [5,6] or Paul [7–10] varieties. The present apparatus is designed to exploit the best features of each by combining the guided ion beam arrangement with ion trapping techniques in order to design and construct an apparatus which both accumulates and stores selected ionic collision products at densities which can exceed 10^8 cm^{-3} for arbitrarily long time periods. The main component is a linear, radiofrequency (rf), quadrupole ion trap where particle collisions, accumulation, and product detection are carried out. In addition, the apparatus includes ion and atom beam generation

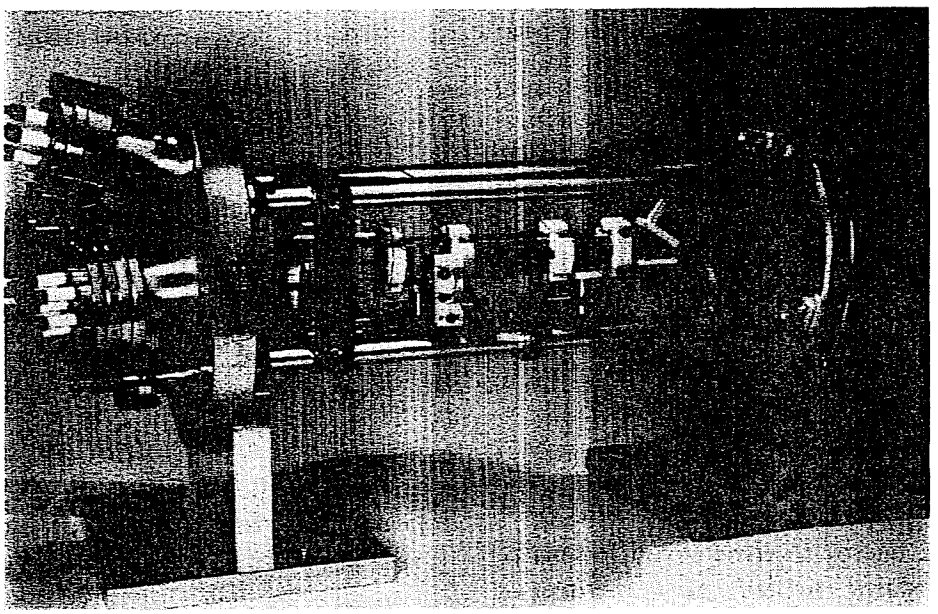

Fig. 1. Photograph of the linear-geometry ion trap apparatus mounted on its vacuum flanges showing the trap electrodes, atomic and molecular ovens, and electron guns. The external ion source is located at the right end of the trap and can be identified by its curved focusing electrode. The scale of the photo is indicated by the 15 cm total length of the trap electrodes.

sections. The collision energy can be controlled over a variable range. The lower limit is below 3 eV and depends mainly on the ion generation technique. The maximum ion kinetic energy depends on the region of interest, and is presently 200 eV. In general, all ionic collision products within a selected mass range will be collected in the trap due to its large well depth, which can reach several hundred eV for light ions. In addition, by either employing a mass-selective parametric excitation of the ion's harmonic motion with a suitable quadrupole field, or varying the stability regime of the trap, both of which are dependent on charge to mass ratios, it is possible to filter out unwanted ionic species. In this way, pure samples for analysis, as well as mass-resolved spectra of the trap population, can be generated. The former technique yields high resolution spectra over a narrow mass range, while the latter approach produces lower resolution spectra that cover the entire range of trapped masses in a single short sweep. Parametric secular excitation mass spectrometry is introduced as a complementary alternative to the more traditional techniques of quadrupole mass spectrometry [11], Fourier transform ion–cyclotron resonance mass spectrometry in Penning traps [6,12–14], or time-of-flight mass spectrometry [15,16]. The accumulated atomic and/or molecular ions can be stored for periods as long as several hours. This permits systematic optical spectroscopic measurements, such as laser-induced fluorescence (LIF) or photodissociation of vibrationally and rotationally relaxed species, to be carried out. LIF can be observed with a sensitive photon detection system which is capable of single ion detection. In general, both absolute and partial photodissociation cross-sections have been studied by employing both mass spectrometry and optical spectroscopy. Both were demonstrated in fragmentation studies of MgC_{60}^+, and were shown to permit the measurement of very slow dissociation rates. In these experiments, the spectral resolution was improved by cooling the translational ion motion with viscous drag forces in a dilute buffer gas. Modern laser cooling techniques such as Doppler cooling were also demonstrated with atomic ions, and should, in addition, be effective for cooling molecular ions via sympathetic processes [17]. Finally, by accumulating projectile ions inside the trap, it was possible to study multibody collision processes. Experiments involving collisions between C_{60} fullerenes, electrons, Mg^+ ions and noble gas atoms have been used to demonstrate the operation of this system. Detailed analysis and more complete data of this work are presented elsewhere [18–21].

2. Theory of ion manipulation with electric fields

2.1. Ion storage in rf quadrupole fields

The theory of trapping charged particles with oscillating electric quadrupole fields is well documented [22,23], and therefore this discussion will be restricted to the case of an ion trap with a linear geometry. The conceptually easiest approach is a treatment of the particle's equation of motion in the adiabatic approximation [24]. This allows for the separation of the motion into two parts: a fast driven oscillation at the frequency Ω of the applied rf field, the so-called micromotion, and a slower, secular motion within the effective pseudopotential of the trapping field. The amplitude of the micromotion increases with increasing radial displacement $\rho=(X^2+Y^2)^{1/2}$ from the central, longitudinal Z-axis, where the X- and Y-axes are the transverse axes of the quadrupole field. The secular amplitude depends on the kinetic energy of the stored ions and is in this way temperature dependent.

For a particle with charge ze and mass m, moving in a two-dimensional oscillating quadrupole field ψ of the form

$$\psi(x, y, z, t)=\psi(t)\frac{X^2-Y^2}{2r_0^2} \quad (1)$$

$$\psi(t) = U_{rf} \cdot \cos \Omega t, \quad (2)$$

the time-averaged pseudopotential Ψ is harmonic and is given by

$$\Psi(\rho) = \frac{z^2 e^2 U_{rf}^2}{4m\Omega^2 r_0^2} \frac{\rho^2}{r_0^2} = \Psi_0 \frac{\rho^2}{r_0^2} \quad (3)$$

The depth of the trap is denoted by Ψ_0, and $2r_0$ is equal to the distance between two non-adjacent quadrupole trap electrodes. The motion of the ion in the Z-direction is that of a free particle.

The oscillatory secular motion of the ion in the pseudopotential is mass dependent, with the frequency of the motion given by

$$\omega_{sec} = \frac{1}{\sqrt{8}} q\Omega \quad (4)$$

where the dimensionless parameter q, containing dependences on particle mass and rf field parameters, is given by

$$q = 2 \frac{z}{m} \frac{1}{\Omega^2} \frac{eU_{rf}}{r_0^2} \quad (5)$$

The complete theory of this problem [22,23] is expressed in terms of the well known Mathieu differential equation and also includes a second parameter, a, related to an additional DC term in Eq. (2). However, the experiments reported here did not employ a quadrupole DC voltage, and thus the parameter a has been set to 0 and does not appear in eqns (3)–(5) for ease of understanding.

The fundamental requirement for stable trapping is that the amplitude of motion of the particle must be finite and limited. The general solution of the Mathieu equation reveals the existence of both stable and unstable solutions, determined exclusively by the parameters q and a (see for example Figs. 2 and 3 in ref. [23]). In other words, the parameter space of q and a is subdivided into regions of stable trapping and unstable particle motion. The region of stability used in this work is the one closest to the origin, and requires $|q| \leq 0.908$ for $a = 0$.

A lower limit on the potential depth of the trap arises from the experimental goal of accumulating the products of ion–molecule collisions. Potential depths below the kinetic energy of the collision products allow the products to escape. In the case of a collision between a heavy, evaporated molecule (e.g. C_{60}) with low kinetic energy, and an atomic ion A^+, an estimate of the kinetic energy of the product complex AC_{60}^+ is given by

$$E_{kin}(AC_{60}^+) = \tfrac{1}{2} m_{AC_{60}} \cdot v_{AC_{60}}^2 = \tfrac{1}{2} \frac{m_A^2}{m_{AC_{60}}} \cdot v_A^2 = \frac{m_A}{m_{AC_{60}}} E_{kin}(A^+) \quad (6)$$

As an example, collisions between thermal C_{60} and $^{24}Mg^+$ result in only 3.2% of the collision energy being transferred into kinetic energy in a generated MgC_{60}^+ complex. The rest of the collision energy produces internal excitation of the complex. Therefore, for the accumulation of these complexes, it is sufficient to generate a pseudopotential with a depth for MgC_{60}^+ in excess of $m_{Mg}/m_{MgC_{60}}$ times the collision energy. At the same time it is essential to quickly remove the excess internal excitation energy, for example by viscous collisions with a buffer gas, in order to prevent the complex from disintegrating.

The above discussion describes the two-dimensional dynamic trapping in the X- and Y-directions by an oscillating rf quadrupole field. Additional confinement in the Z-direction could also be achieved by oscillating inhomogeneous fields, but is impractical in the present case, since it does not allow for the efficient injection of projectile ions into the trap or the creation of a well defined collision energy. The alternative approach, which was developed here, is to use static fields to confine the ion's motion in the Z-direction. Two DC-confinement electrode arrangements are employed. In one, confinement is achieved by subdividing the four quadrupole trap electrodes into three adjacent, but electrically isolated, segments. Different DC potentials are then applied to the three segments such that a square well potential is created in the Z-direction

(Fig. 2(b)). It should be pointed out that the generated confinement fields are not quadrupolar in nature, since the same DC potential is applied to all four electrodes in one segment. The other approach is to confine the ions in the Z-direction by applying DC potentials to small endcap electrodes suspended at either end of the trap. Both arrangements allow for selectivity between positively and negatively charged particles, a freedom which is not present with charge-insensitive rf trapping fields. In the present experimental set-up, a combination of these fields is used to provide efficient injection of ions into the trap, as is described in Section 3.

2.2. Mass spectrometry and mass-selective expulsion

Most of the trapping parameters are mass dependent. Thus the rf-quadrupole ion trap is a natural mass filter. This mass selectivity can be used either to purify stored samples by expelling unwanted masses or to record accurate mass spectra by detecting the masses as they are expelled. This section will outline three mass-selective expulsion techniques which have been utilized, in combination or individually, for a variety of different purposes.

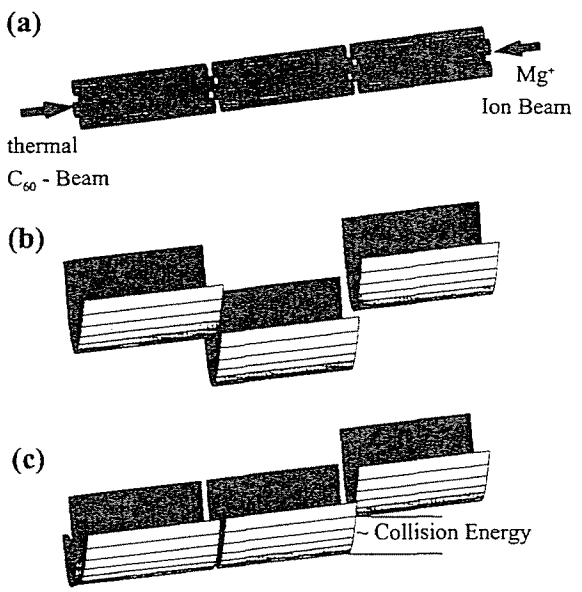

Fig. 2. Trap electrode configuration (a) and time-averaged pseudo-potentials for (b) ion storage and (c) ion–molecule collisions. The latter demonstrates how the collision energy is controlled in these reactions.

The first technique is the approach common to many quadrupole mass spectrometers, in which the trap stability parameters are varied to move selected masses from the stable to the unstable regions of (q, a)-parameter space (see Fig. 2 in ref [23]). As stated earlier, for $a=0$ the stability region nearest the (q, a) origin requires $|q| \leq 0.908$. Therefore, for a given U_{rf} and Ω, all masses given by

$$\frac{m}{z} < 2.203 \frac{eU_{rf}}{r_0^2 \Omega^2} \tag{7}$$

are destabilized out of the trap. This lower mass limit could be used to take mass spectra by gradually increasing U_{rf} or reducing Ω, although other techniques were employed in this system. It was used in this work to set a lower limit on the masses collected by the trap. Due to the inverse mass dependence of q (see Eq. (5)), there is a low mass threshold below which masses escape from the trap, but no upper limit when $a=0$. Employing an additional quadrupole DC voltage ($a \neq 0$) can be useful because it results in an upper limit on the ionic mass for stable trapping. Only those masses between the low and high mass limits are trapped. By operating the trap near the tip of the stability region, trapping of a narrow range of masses is permitted. This is the technique used in an rf quadrupole mass filter. However, it is not the appropriate method to determine a mass spectrum from samples trapped for long time periods, because the case of a (q, a) combination close to the border of the stability regime results in strong rf heating, which leads to very short storage times [25].

The second technique, referred to as q-scanning, has been developed to obtain low resolution mass spectra over the complete range of masses stored in the trap in a short time. The method uses a perturbative static electric field to provide a lower limit to the stability region of (q, a)

parameter space, which corresponds to an upper limit on the stored masses. Although a complete theoretical description of this method would require more complexity than the Mathieu equation model, it is possible to provide a rough theoretical description in terms of the stability diagram for the Mathieu equation and the related pseudopotential. In the preceding discussion it was stated that for $a=0$ there is no lower limit on the stability diagram and that masses remain stable as q approaches 0. However, the trap depth is also proportional to q and thus, at low q's, any small perturbing forces can empty the trap. For example, if a homogeneous electric field ε is applied perpendicular to the Z-axis, then an estimate for the threshold above which masses are pulled out of the trap is expressed by the condition that the force due to the external field exceeds the force from the trapping field. Combining this condition with Eq. (3) yields the following approximate lower bound for ion expulsion:

$$\frac{m}{z} > \frac{1}{2}\frac{eU_{rf}^2}{\varepsilon r_0^3 \Omega^2}. \tag{8}$$

This approach can be used to set an upper limit on the collected masses, or it can be used to take a mass spectrum by detecting the ions pulled out of the trap as the parameters U_{rf} or Ω are varied. The generated spectrum will always appear from high to low masses. Although the resolution with this approach is only moderate, the technique is valuable because of the wide mass ranges which can be quickly observed. Moreover, in the present work the electric field ε is simply generated by negatively biasing the front cathode of the external ion detector, as is described further in Section 3.

The third technique has been implemented to yield the highest resolution mass spectra that we generate with this apparatus, and is referred to as secular scanning. Rather than exploiting the stability thresholds in (q, a)-parameter space, this approach is based on direct, parametric excitation of the classical ion motion within the harmonic pseudopotential (Eq. (3)). An ion of mass m oscillates at its secular frequency ω_{sec} as given by Eq. (4). In principle, this oscillation could be excited by a homogeneous and/or a mixed multipolar, oscillating, electric field with frequency $\omega_{exc} = \omega_{sec}$ (e.g. [9,26,27]), but the particular geometry of the trap electrodes suggests an alternative approach in which the ion motion is driven as a parametric oscillator. This requires a quadrupole excitation field with frequency $\omega_{quad} = 2\cdot\omega_{sec}$, which can be generated simply by applying an additional oscillating voltage at frequency ω_{quad} to the trap electrodes. Parametric excitation with a pure quadrupole field offers both theoretical and experimental advantages over the previously demonstrated mixed multipolar field excitation techniques [9,26,27]. One theoretical advantage is the possibility of modeling this method on the basis of the well known theory of parametric excitation [28], while a more practical advantage is the reduction in the number of possible resonances for an ion with a given charge to mass ratio. The mass which is selected with a given ω_{quad} is

$$\frac{m}{z} = \sqrt{2}\frac{eU_{rf}}{\omega_{quad} r_0^2 \Omega}. \tag{9}$$

If the driving field is applied for a sufficient time period, the ion is driven out of the trap. High resolution mass spectra can be taken by slowly scanning ω_{quad} and simultaneously counting the escaping ions. The resolution of this system depends both on the width of the parametric resonance [28] and on the frequency dependence of the energy deposition rate of the secular excitation process. The latter mechanism is highly dependent on the scanning rate during the collection of spectra. The secular excitation technique can also be used to drive any selected mass range out of the trap in order to purify a sample before experimentation by scanning ω_{quad} over the required frequency range calculated by Eq. (9).

3. Experimental apparatus and general procedures

Fig. 1 shows a photograph of the linear ion trap which has an overall electrode length of 15 cm. The quadrupole electrodes are depicted in Fig. 2(a). They are constructed out of 6 mm diameter, non-magnetic, stainless steel, cylindrical rods. The ratio of the electrodes' diameters to their diagonal spacing (5.22 mm) was chosen to be 1.146 in order to minimize higher order multipole contributions to the trapping field [29]. The trapping field used in this work had a maximum amplitude of about 3 kV at a constant frequency of 8.55 MHz. This feature permitted simultaneous transverse trapping of ions over the broad range of masses from 20 to over 4000 u, in a mass-dependent potential greater than 1 eV. For example, with a trap amplitude of 2 kV, the potential depths for $^{24}Mg^+$ and MgC_{60}^+ are 248 eV and 8 eV, respectively. In order to generate an rf trapping field with the required amplitude, the trap itself forms part of a resonance circuit. The circuit for operating the linear-geometry trap is shown schematically in Fig. 3. It includes the trap itself as the capacitor (~45 pF) which is combined with an inductor coil (~8 μH) mounted outside the vacuum chamber. The electrical connections to the trap are designed to allow for the generation of identical rf quadrupole fields on all three segments of the trap simultaneously while independent, non-quadrupole, DC fields can be applied to each segment. A quality factor Q of about 80 has been achieved for the tank circuit by using a low-loss Teflon core for the inductor coil, as well as for the high voltage, low pass, filter coils. The rf amplitude is actively stabilized to a relative variation of less than 0.05%. This is required for high resolution mass spectrometry because the secular frequency is proportional to the rf amplitude.

In order to control the ion motion along the longitudinal axis of the trap, adjustable potential steps can be generated due to the subdivision of all four quadrupole electrodes into three adjacent but electrically isolated segments, each 50 mm in length. Applying different DC potentials to the resulting three trap segments (see Section 2.1) permits either the generation of a square well potential for ion storage or the acceleration (or deceleration) of ions moving from one segment

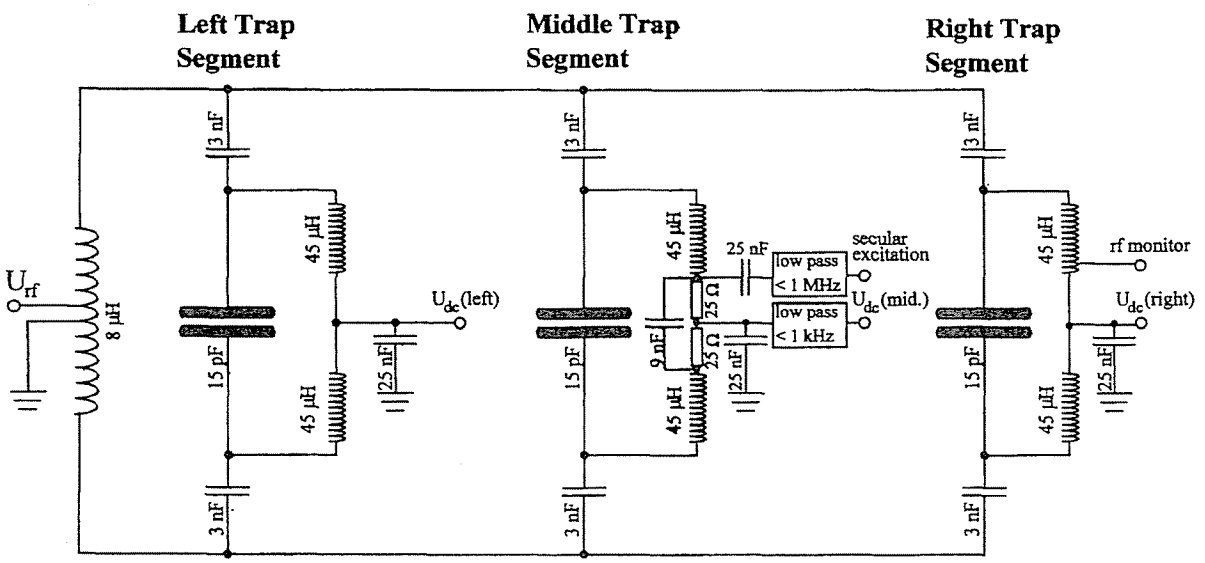

Fig. 3. Schematic diagram of the trap and electric filtering circuits. The center of the diagram illustrates how the secular excitation field is applied only to the center segment of the trap.

to the adjacent one (Fig. 2). Potential steps as large as 200 eV are possible with the present experimental arrangement. The space between the electrodes of two adjacent trap segments is only 0.1 mm in order to minimize any perturbations in the quadrupole rf trapping field and to match the phase of the rf trapping fields in all three segments. The electrodes making up the left and right outer segments of the trap are held in position by macor spacers. However, the center segment electrodes are not mounted on their own spacers, but instead are connected directly to the ends of the outer electrodes with ceramic spheres which fit into holes drilled into the ends of the electrodes. These spheres hold the center electrodes in place while maintaining electrical isolation. This kind of suspension reduces the possibility of disturbances of the ion motion in the center segment resulting from surface charge buildup on the spacers. Simultaneously, the lack of large spacers in the central region of the trap allows for easier access to the trapped ions for measurement purposes. For instance, the opening angle of 25.4° for LIF detection is limited only by the electrode spacing and not by any mounting pieces.

The separation of the quadrupole electrodes into three adjacent segments only allows for trapping in the center segment. In order to introduce more flexibility to the apparatus by permitting trapping in the outer segments as well, additional longitudinal potential steps can be generated by biasing small tubular electrodes mounted on the central axis at either end of the trap. The use of tubular end electrodes also allows access to the central trap axis, which is useful for laser illumination of a trapped ion cloud collinear with the long axis. In these experiments, use of the tubular electrodes for efficient injection of neutral and ionic beams into the collision region of the trap prevents laser access directly along the trap axis. Injection of ions along the trap axis is ideal because the kinetic energy can be conserved only under conditions of zero rf field, which occurs along the trap axis inside and outside the trap when equal-amplitude rf fields are applied in the X- and Y-directions (see Eq. (1)). Experimentally, this condition was achieved by using one of the end-cap electrodes as a pick-up loop to measure the rf field on the central axis. The grounding point on the external inductor coil was adjusted while the antenna signal was minimized. Although, in the present setup, the atomic and molecular ovens block the trap axis, it is still possible to direct a laser beam off axis between the trap electrodes and irradiate ions stored in the center section of the trap. The selected angle of incidence of the laser beam with respect to the trap axis is 15°.

The method of choice for ion generation depends on the desired ion species and other experimental needs such as kinetic energy resolution or ion beam intensity. In general, any type of ion source could be employed in combination with this compact linear ion trap. There are two approaches which are generally used in our experiments. In the first one, ions are generated inside one of the outer trap segments by crossing a collimated atomic beam with an ionizing electron beam. The two beams are at right angles to each other and pass separately through the spacings between the trap electrodes. This is a simple technique to implement, but the ion collection and generation efficiencies are relatively low and there is little control over the initial kinetic energy of the trapped ions. The second method provides higher injection and generation efficiencies and better kinetic energy control, but requires additional focusing electrodes not required for the preceding technique. Ions are produced by electron bombardment of an atom beam outside one end of the ion trap. Focusing electrodes (Fig. 4, inset) biased with applied DC fields are used to inject the ions along the trap axis. In addition, the injection electrodes can be used to cut off the low kinetic energy fraction of the generated ions by generating a step potential at the input end of the trap. This simple ion source generated a broad kinetic energy spectrum peaked at approximately 4 eV, with a width of

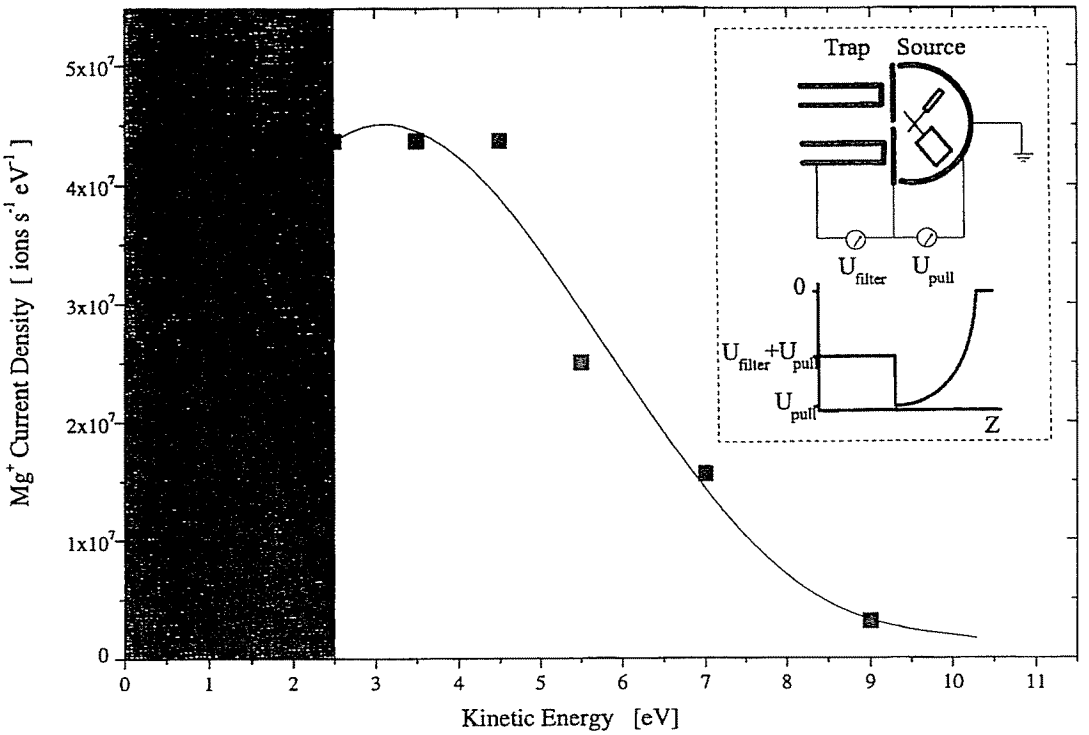

Fig. 4. Kinetic energy distribution of the ions produced in the Mg^+ ion source. The grey area indicates the ions not injected into the trap due to the filter potential. The inset shows the ion source electrode arrangement used to inject the ions into the trap and to reduce the kinetic energy spread.

about 6 eV (Fig. 4). The energy spread could be reduced to 4 eV with only the indicated loss in ion intensity by applying a 2.5 V cut-off potential.

The results presented in this paper required the generation of Mg^+, rare gas ions, and C_{60}^+. In the cases of Mg and C_{60}, pure samples were evaporated from miniature ovens, which can be heated to their operating temperature in only a few seconds. They consist of a small tantalum or nickel tubes (diameters of 1 or 1.8 mm, respectively) that are closed at one end, filled with the required material in solid or powder form, and then heated by passing a current of approximately 1.5 A through a 0.3 mm diameter tantalum wire which has been spot welded to the tube. The external Mg^+ ion source yields an ion current of up to 200 pA, but more typically was operated at 30 pA. Its performance was limited by a weak electron gun. Without mass filtration the purity of the generated Mg^+ ion beam was better than 10^{-3} due to the high purity of the source materials and the low background pressure inside the UHV chamber. Multiply charged atomic ions, such as Mg^{2+}, which may be produced in small numbers, are not stored in the trap, since their q-value is outside the chosen stability range of the rf trapping field. However, for other background ions the procedures outlined in Section 2.2 could be used to mass-selectively purify the sample. In addition, rare gas ions can be loaded into the trap. Rather than generating a collimated beam of rare gas atoms, the chamber is filled with a low partial pressure of the desired noble gas atom, and then ions are generated using the electron gun in the Mg^+ ion source with the Mg oven turned off.

With this trap it is possible to store more than 10^6 ions, corresponding to an ion density exceeding 10^8 cm^{-3}. The ions can be held in the trap for

periods as long as several hours. Once a sample has been loaded into the trap, probing and analysis can be carried out with mass spectrometry and/or laser irradiation spectroscopy. Quartz windows in the vacuum chamber allow ultraviolet (UV), visible (vis) and infrared (IR) radiation to probe the trapping volume. Resonance fluorescence was observed by high sensitivity photon detection using a collimating objective and a photomultiplier tube (PMT) positioned perpendicular to the trap axis (Fig. 5). Accurate imaging through suitably located spatial and bandpass filters was used to reduce the detection of radiation scattered directly from the trap electrodes and the walls of the vacuum chamber. These measures improved the signal to noise ratio to the point where single ions could be easily detected. Furthermore, the LIF signal was used to optimize the overlap of the employed laser beams with the trapped ion cloud. Specifically, Mg^+ was used in these experiments because of its strong resonance line at 280 nm ($3^2S_{1/2} \rightarrow 3^2P_{3/2}$). The first step was to load the trap with Mg^+ so that the 280 nm laser beam path could be overlapped with the ions by maximizing the LIF signal. All other laser beams would then be overlapped with this path by precise matching of the pointing and focal position. The laser beams were all gaussian in cross-section, and were focused down to beam waists of 90–100 μm at the centre of the trapping volume. Light resonant with the $3^2S_{1/2} \rightarrow 3^2P_{3/2}$ transition of Mg^+ was generated by doubling the output from a cw ring dye laser with a KDP crystal positioned inside an external intensity enhancement cavity. The system provided a maximum of 30 mW of UV power, but LIF from Mg^+ was already observable with incident powers well below 1 mW.

The mass spectrometric techniques discussed in Section 2 require the detection of ions ejected from the trap. We employed a simple, compact set-up consisting of an electron multiplier tube (EMT) mounted adjacent to the trap electrodes and perpendicular to the trap axis. For high collection efficiencies it was displaced from the trap by merely 15 mm (Fig. 5). Positively charged ions were detected by biasing the front cathode of the EMT at -3.5 kV. In the q-scanning mode, ions for which the potential depth is less than

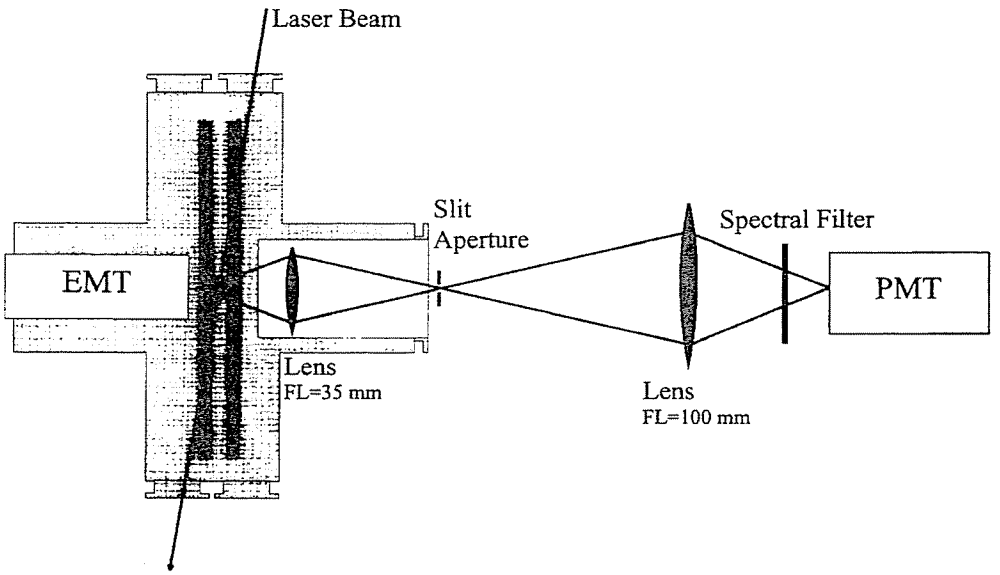

Fig. 5. Diagram of the ion trap inside its vacuum chamber indicating the laser beam path, the optical system for fluorescence collection and detection with a photomultiplier tube (PMT), and the position of the electron multiplier tube (EMT) for ion detection.